

Perchlorate Analysis by Ion Chromatography

The CA DHS Protocol

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Disclaimer

- ' Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Topics

- ' Equipment
- ' Eluent Composition Study
- ' Linear Calibration Range
- ' MDL Study
- ' Interferences
- ' Sample Collection and Preservation
- ' Method Performance
- ' Method Advantages
- ' Method Limitations
- ' Additional Needs

Equipment

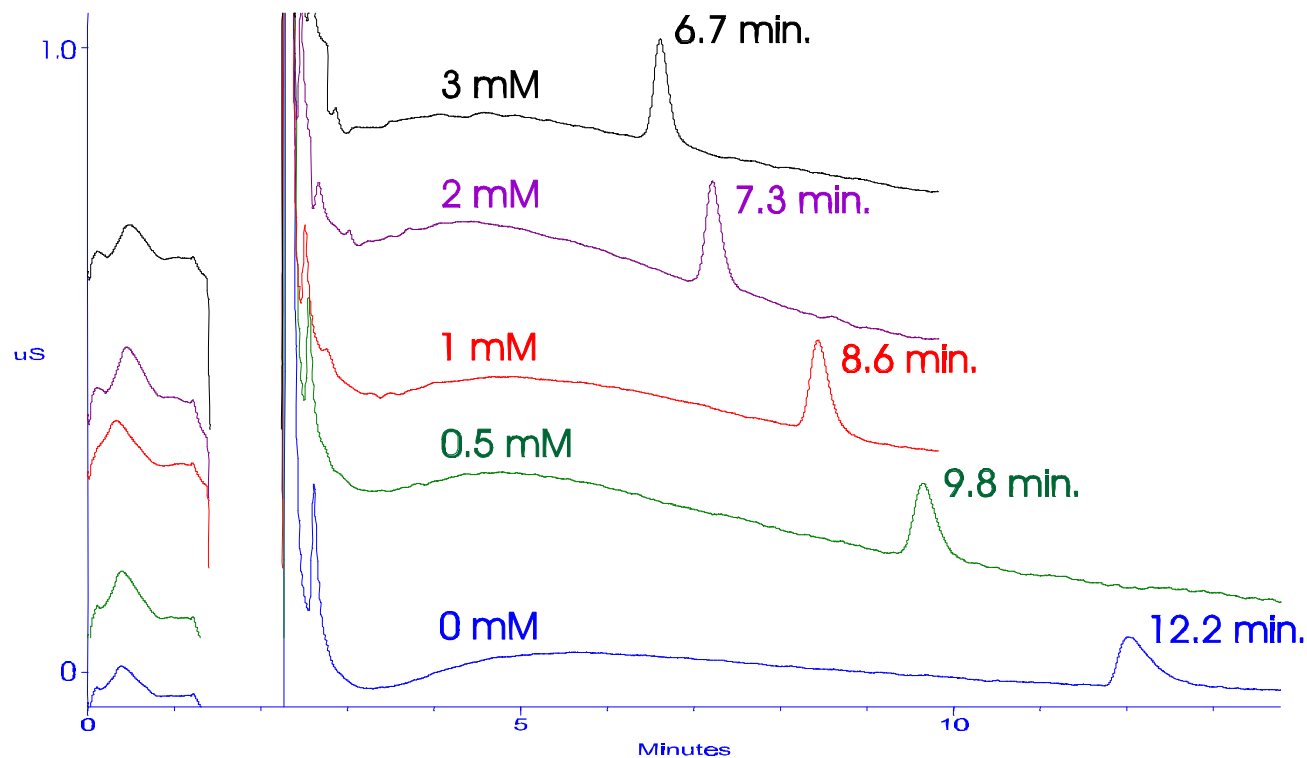
- ' Ion chromatograph: autosampler, dual piston pump, ion suppressor, conductivity detector and data system.
- ' Sample loop: 740 μL (12' x 0.02" tubing)
- ' Column: Dionex IonPac® AS5 (4 x 250 mm)
- ' Chemical regenerant: Dilute sulfuric acid
- ' Eluent: 120 mM NaOH + 2 mM p-cyanophenol

Eluent Composition Study

- ' High concentration of NaOH (120 mM) is employed in the eluent.
- ' p-Cyanophenol modifier must be added to the eluent to deactivate the AS5 ion exchange column.
- ' In initial tests, the p-cyanophenol concentration was varied while maintaining the NaOH concentration at 120 mM.

Effects of p-Cyanophenol on the Elution of ClO_4^-

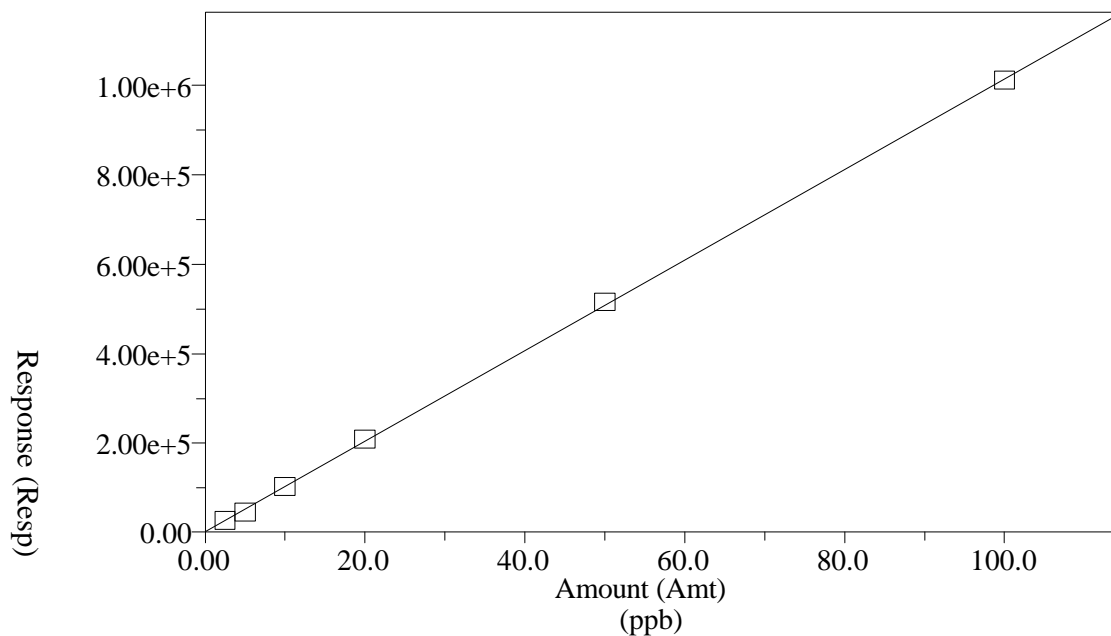
- ' 15 ppb Perchlorate
- ' Eluent: 120 mM NaOH + X mM p-Cyanophenol



Linear Calibration Range

2.5 to 100 ppb Perchlorate

Component: Perchlorate; Fit Type: Linear
Method: c:\clo4.met; Updated: 3/27/98 2:46:19 PM
 $r^2 = 0.999828$
 $\text{Amt} = 9.868\text{e-}005 * \text{Resp} + -0.1764$
Standard: External
Calibration: Height



MDL Study

ClO_4^- Spike Conc. ($\mu\text{g/L}$)	No. of Spiked Replicates	Mean Recovery ($\mu\text{g/L}$)	SD ($\mu\text{g/L}$)	Calculated MDL ($\mu\text{g/L}$)
2.5	16	2.3	0.12	0.8
4.0	16	3.9	0.11	0.7

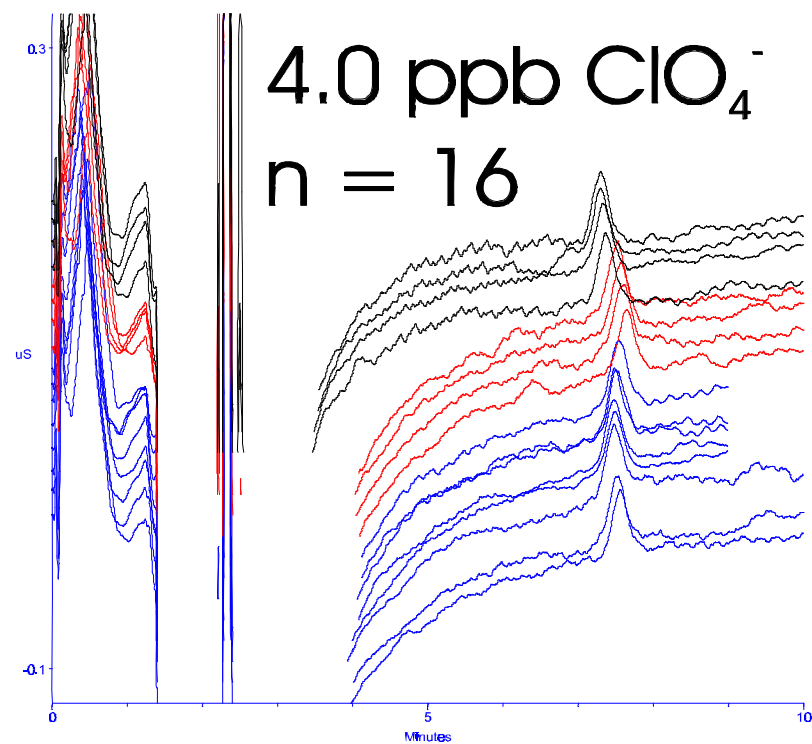
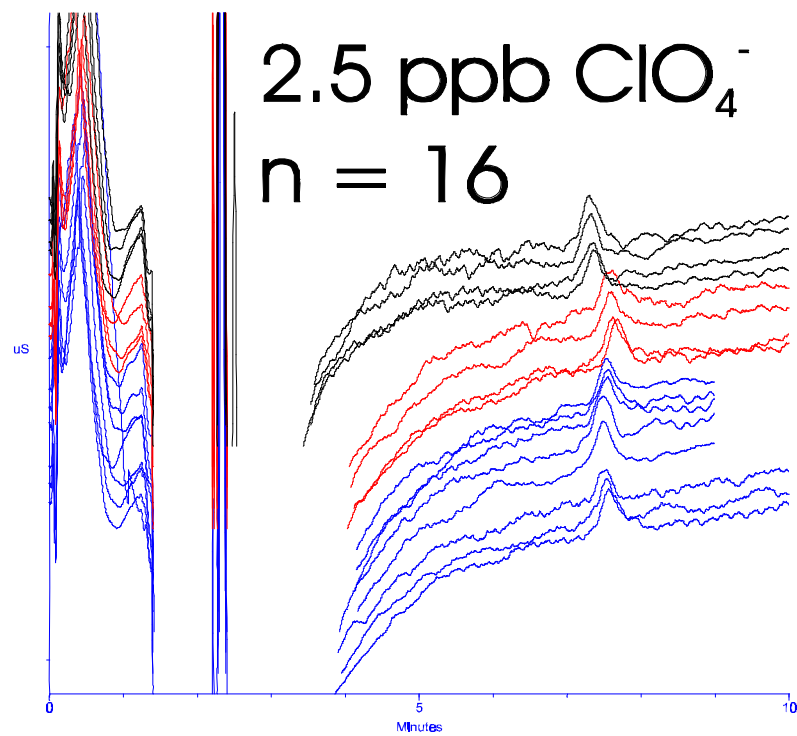
Pooled MDL (df = 30)	0.7 $\mu\text{g/L}$
Reporting Limit (5 x MDL)	4 $\mu\text{g/L}$

ClO_4^- Spike Conc. ($\mu\text{g/L}$)	No. of Spiked Replicates	Mean Recovery ($\mu\text{g/L}$)	SD ($\mu\text{g/L}$)	RSD (%)
0	16	n/a *	n/a	n/a
1.0	16	0.8 **	0.4	50

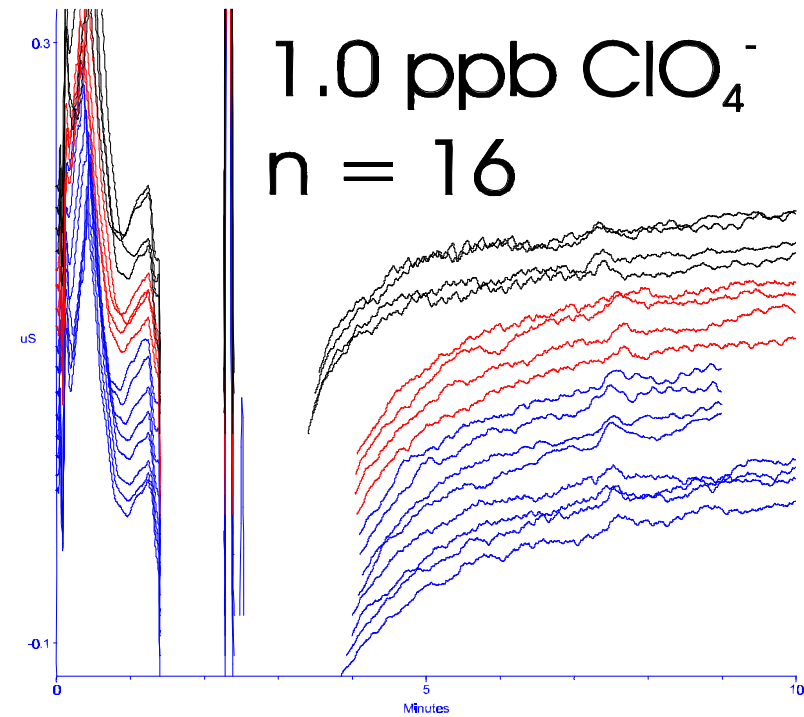
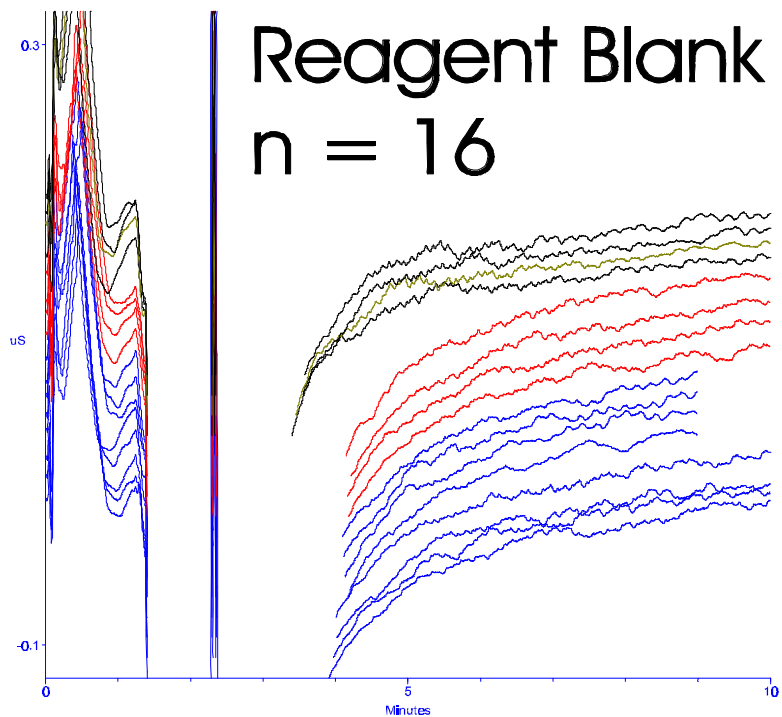
* One false positive result of 0.7 $\mu\text{g/L}$.

** Includes 2 false negative results.

MDL Study



MDL Study



Interferences

- ' Pump noise (pressure pulses) - oscillating baseline.
- ' Air bubbles trapped in the pump head or conductivity cell -- baseline spikes and/or oscillating baseline.
- ' Improperly adjusted chemical suppression -- high background conductivity, low perchlorate response.
- ' Detergents and other organics -- column, suppressor and detector fouling.
- ' High sample TDS -- column and detector overload; may severely affect baseline response.

Anions Known Not to Colute with Perchlorate

Arsenate	Cyanide	o-Phthalate
Arsenite	Humic Acid	Selenate
Bromate	Iodate	Sulfate
Bromide	Iodide	Sulfite
Carbonate	Molybdate	Thiocyanate
Chlorate	Nitrate	Thiosulfate
Chloride	Nitrite	
Chromate	o-Phosphate	

Sample Collection and Preservation

- ' Sampling container: HDPE plastic bottles
- ' Sample storage: store at 4°C
- ' Holding time: 28 days (likely to be more)

Holding Time Study - Stored at 4°C

Well ID.	Date Collected	Conduct. $\mu\text{S/cm}$	Initial Hold: 6-11 Days	Holding Time 54 Days	Holding Time 70-71 Days
MAFB #4MB	3/25/97	120	ND		ND
	4/10/97	120	ND	ND	
SCWC #14	3/24/97	300	4.4		~3.9 (-11%)
	4/10/97	250	4.0	4.8 (+20%)	
SCWC #19	3/24/97	180	6.8		7.8 (+15%)
	4/10/97	300	7.6	7.7 (+1%)	
MAFB #3MB	3/25/97	120	14		15 (+7%)
	4/10/97	120	16	16 (0%)	
MAFB #1MB	3/25/97	120	67		68 (+1%)
	4/10/97	120	72	72 (0%)	
SCWC #13	3/25/97	260	260		250 (-4%)
	4/10/97	320	250	230 (-8%)	

Holding Time Study

- Tap water sample fortified with perchlorate
 - Stored for 10 months at 4°C
 - Stored for 10 months at room temperature

Sample Conductivity	Initial ClO_4^- Conc.	Storage Temperature	ClO_4^- Conc. after 10 Months
840 $\mu\text{S}/\text{cm}$	18.1 \pm 1.3 $\mu\text{g}/\text{L}$ (n = 8)	4°C	19.3 \pm 0.3 $\mu\text{g}/\text{L}$ (n = 3)
		Room Temp.	19.4 \pm 0.3 $\mu\text{g}/\text{L}$ (n = 3)

Method Performance

Single Operator Accuracy and Precision

Sample Type	Sample Matrix	ClO ₄ ⁻ TV (µg/L)	No. of Repl.	ClO ₄ ⁻ Mean Recovery		SD (µg/L)	RSD (%)
				(µg/L)	(%)		
IPC	Reagent Water	5.0	105	5.1	102	0.4	7.2
		100	102	103	103	4.6	4.5
Alternate Source Material	Reagent Water	4.0	34	4.0	101	0.3	7.2
		15	3	15	100	1.2	8.0
		100	4	100	100	2.8	2.8
LFB	Reagent Water	4.0	54	4.1	102	0.3	8.3
		15	6	15	100	0.5	3.4

Method Performance

- ' Sample Duplicate Analysis & MS/MSD
- ' Single Operator Accuracy and Precision

Sample Type	Sample Matrix	No. of Replicate Pairs	Mean RPD (%)	SD of Mean RPD (%)
Sample/Sample Duplicate: 4 to 260 µg/L of ClO ₄ ⁻	Groundwater	18	1.3	1.9

Sample Type	Sample Matrix	Spike Conc. (µg/L)	No. of Spiked Pairs	Duplicate Spike Mean Recovery		Mean RPD (%)	SD of Mean RPD (%)
				(µg/L)	(%)		
MS/MSD	Groundwater	4	47	4.1	103	7.7	6.1

Inter-Laboratory Performance

- ' Tap Water
- ' Conductivity = 840 $\mu\text{S}/\text{cm}$
- ' ClO_4^- TV = 18.1 $\mu\text{g}/\text{L}$
- ' Acceptable Range: 14.3 - 21.9 $\mu\text{g}/\text{L}$

- ' No. of Labs = 11
- ' Mean Value Reported = $18.6 \pm 1.8 \mu\text{g}/\text{L}$

Method Performance

- ' Capable of meeting the QC requirements in EPA 300.0 for ion chromatography:
 - ' QCS result within $\pm 10\%$ of known value.
 - ' Instrument performance check solution results within $\pm 10\%$ of calibration.
 - ' Method blank results less than the MDL.
 - ' Lab fortified blank results within control limits of 90 - 110%.
 - ' Laboratory fortified sample matrix recovery results within 80 to 120%.

Method Advantages

- ' Uses current technology that is available in many water utility and commercial analytical laboratories.
- ' Based on EPA 300.0 - many analytical laboratories are familiar with the QA/QC requirements.
- ' Requires very little sample preparation for drinking water samples.
- ' Quick and easy to perform.
- ' Provides the sensitivity required for the current California DHS provisional action level of 18 ppb in drinking water.

Method Limitations

- ' Requires a large sample volume of 740+ μL to achieve the necessary sensitivity.
- ' Due to the large sample volume, high TDS in a sample may cause interference in the detection and/or quantification for perchlorate at very low levels.
- ' High TDS in a sample may also cause column, suppressor, and/or detector fouling that can result in a noisy and unstable baseline.
- ' AS5 column activity causes perchlorate to tail without a modifier (p-cyanophenol) added to the eluent.

Additional Needs

- ' Need for confirmatory procedures, including identification.
- ' Need for improved detection limits.
- ' Need for clean up methods.
- ' Need to keep method simple and transferable to water utility and commercial analytical laboratories.
- ' Need for a more comprehensive storage and holding time study.
- ' Need for a more comprehensive inter-laboratory performance study.

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- ' Haddad, P.R. & Jackson, P.E., Ion Chromatogr.: Principles and Applications, J. Chromatogr. Lib. 1990: 46:Ch. 4.
- ' CFR 40, Ch. 1, Part 136, Appendix B
- ' US EPA Method 300.0: Determination of Inorganic Anions by Ion Chromatography, Rev. 2.1, Aug. 93

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